(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 0 919 126 A1

# (12) EUROPEAN PATENT APPLICATION

published in accordance with Art. 158(3) EPC

(43) Date of publication:
**02.06.1999 Bulletin 1999/22**

(21) Application number: **97924304.5**

(22) Date of filing: **03.06.1997**

(51) Int. Cl.[6]: **A01N 37/52**, A01N 43/60, A01N 37/36, A01N 43/32, A01N 37/38, A01N 37/50, A01N 43/40, A01N 43/82, A01N 43/38, A01N 43/54

(86) International application number:
**PCT/JP97/01880**

(87) International publication number:
**WO 97/46097 (11.12.1997 Gazette 1997/53)**

(84) Designated Contracting States:
**AT BE CH DE DK ES FI FR GB GR IE IT LI LU MC NL PT SE**

(30) Priority: **04.06.1996 JP 163743/96**

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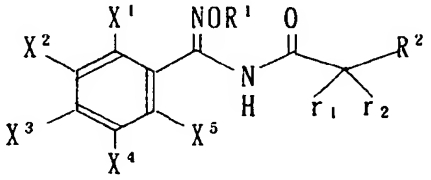
## (54) NOVEL AGRICULTURAL/HORTICULTURAL BACTERICIDAL COMPOSITIONS

(57) The present invention is directed to bactericidal compositions for agricultural and horticultural use, characterized in that the composition comprises a benzamidoxime compound represented by a general formula [I];



. . . [ I ]

wherein $R^1$ represents alkyl, alkenyl, etc., $R^2$ represents phenyl, heterocycle, etc., $X^1$ represents haloalkyl, $X^2$, $X^3$, $X^4$ and $X^5$ each independently represent hydrogen, halogeno, alkyl, etc.. $r_1$ and $r_2$ each independently represent hydrogen, halogeno. alkyl, etc., and a so-called acrylate bactericide as the active ingredients. The bactericidal compositions according to the present invention are combination compositions of bactericidal components, which can improve bactericidal activity obtainable with each component in the combination with a less dose in total of each components.

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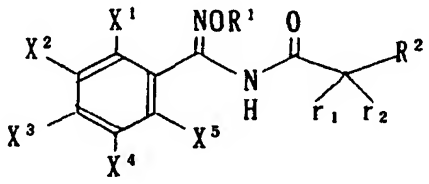
## Description

Field of the Invention

**[0001]** The present invention is directed to bactericidal compositions, particularly to bactericidal compositions suitable to control powdery mildew disease growing on various agricultural and horticultural crops.

Background Art

**[0002]** Benzamidoxime derivatives represented by a general formula [I] ;



[ I ]

are the compounds which has bactericidal activity and are disclosed in WO 96/19442 Gazette filed by the inventors of the present invention.

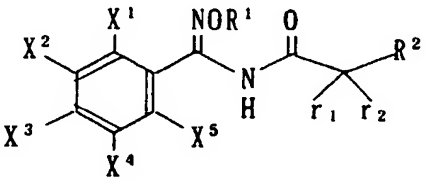
**[0003]** Whereas, so-called acrylate bactericides, for example, ICIA 5504, BASF 490, SSF-126. etc. have been known as new type bactericides for agricultural and horticultural use (see EP 477631, EP 253213 and EP 38237 Gazettes).

**[0004]** However, bactericidal compositions comprising a compound represented by a general formula [I] and an acrylate bactericide and capable of providing synergistic activity have not been known yet.

Disclosure of the Invention

**[0005]** It is an object of the present invention to lower the effective dose of the compounds known as having bactericidal activity against plant diseases, to improve their activity spectrum as a bactericide. and to provide bactericidal compositions in combination which can work with the active ingredients at a less dose in total and improve the effective control value with providing synergistic activity.

**[0006]** The present invention is directed to bactericidal compositions characterized in that each compositions comprises a benzamidoxime compound A represented by a general formula [I];



[ I ]

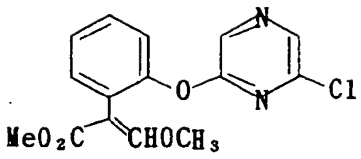
wherein $R^1$ represents optionally-substituted C1-C4 alkyl, optionally-substituted C2-C4 alkenyl or optionally-substituted C2-C4 alkynyl, $R^2$ represents optionally-substituted phenyl or optionally-substituted heterocycle,

$X^1$ represents C1-C4 haloalkyl,

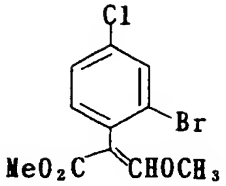
$X^2$, $X^3$, $X^4$ and $X^5$ each independently represent hydrogen, halogeno, C1-C4 alkyl, C1-C4 haloalkyl, C1-C4 alkoxy, C1-C4 haloalkoxy, C1-C4 alkylthio, C1-C4 alkylsulfinyl, C1-C4 alkylsulfonyl, nitro, amino or C1-C4 alkylcarbonylamino,

$r^1$ and $r^2$ each independently represent hydrogen, halogeno, C1-C4 alkyl, C1-C4 haloalkyl, C1-C4 alkoxy, C1-C4 alkylthio or amino, or, $r^1$ and $r^2$ may get together to form carbonyl, and one or more than 2 compounds selected from a group B consisting of the compounds (a) through (n) as shown below as the active ingredients thereof.

B :



( a )



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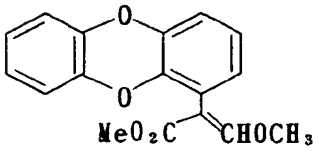

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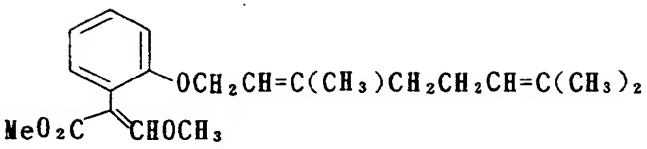
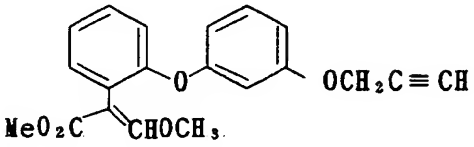


( d )

( e )



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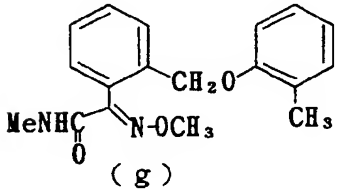

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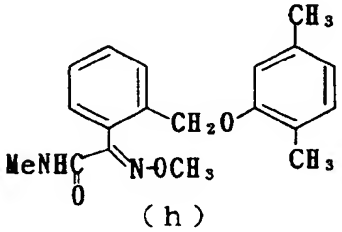
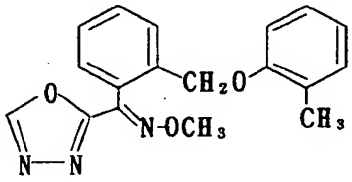
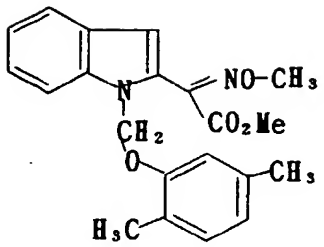


( h )

( i )



( j )



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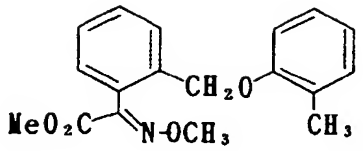


(l)

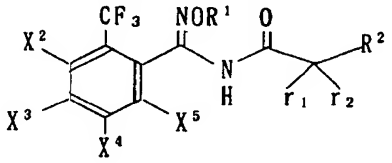
(m)

(n)

**[0007]** The benzamidoxime compounds to be used in the present invention are the compounds represented by the general formula [I] as described above, and one or more than 2 of the compounds can be used as the active ingredient for the bactericidal compositions specified in the present invention.

**[0008]** Preferable examples for the benzamidoxime compounds represented by a general formula [I] are shown in Table 1.

Table 1



( $r_1, r_2$=H )

| No. | $X_2$ | $X_3$ | $X_4$ | $X_5$ | $R_1$ | $R_2$ |
|---|---|---|---|---|---|---|
| 1 | H | H | F | F | $CH_2$-cyclopropyl | Ph |
| 2 | H | H | Cl | F | $CH_2$-cyclopropyl | Ph |
| 3 | H | H | F | Cl | $CH_2$-cyclopropyl | Ph |
| 4 | H | H | Cl | Cl | $CH_2$-cyclopropyl | Ph |
| 5 | H | H | F | F | $CH_2$-cyclopropyl | 2-F-Ph |
| 6 | H | H | Cl | F | $CH_2$-cyclopropyl | 2-F-Ph |
| 7 | H | H | F | Cl | $CH_2$-cyclopropyl | 2-F-Ph |
| 8 | H | H | Cl | Cl | $CH_2$-cyclopropyl | 2-F-Ph |
| 9 | H | H | F | F | $CH_2$-cyclopropyl | 2-F-5-Me-Ph |
| 10 | H | H | Cl | F | $CH_2$-cyclopropyl | 2-F-5-Me-Ph |
| 11 | H | H | F | Cl | $CH_2$-cyclopropyl | 2-F-5-Me-Ph |
| 12 | H | H | Cl | Cl | $CH_2$-cyclopropyl | 2-F-5-Me-Ph |
| 13 | H | H | F | F | $CH_2CH_2Cl$ | Ph |
| 14 | H | H | Cl | F | $CH_2CH_2Cl$ | Ph |

| No. | $X_2$ | $X_3$ | $X_4$ | $X_5$ | $R_1$ | $R_2$ |
|---|---|---|---|---|---|---|
| 15 | H | H | F | Cl | $CH_2CH_2Cl$ | Ph |
| 16 | H | H | Cl | Cl | $CH_2CH_2Cl$ | Ph |
| 17 | H | H | F | F | $CH_2CH_2Cl$ | 2-F-Ph |
| 18 | H | H | Cl | F | $CH_2CH_2Cl$ | 2-F-Ph |
| 19 | H | H | F | Cl | $CH_2CH_2Cl$ | 2-F-Ph |
| 20 | H | H | Cl | Cl | $CH_2CH_2Cl$ | 2-F-Ph |
| 21 | H | H | F | F | $CH_2CH_2Cl$ | 2-F-5-Me-Ph |
| 22 | H | H | Cl | F | $CH_2CH_2Cl$ | 2-F-5-Me-Ph |
| 23 | H | H | F | Cl | $CH_2CH_2Cl$ | 2-F-5-Me-Ph |
| 24 | H | H | Cl | Cl | $CH_2CH_2Cl$ | 2-F-5-Me-Ph |

**[0009]** In the present invention, the acrylate bactericides are defined as bactericidal substances which have been developed from natural substances, such as Oudemansin A and Strobilurine A, as a leading compound and contain any of alkoxymethylene group, alkoxyimino group or the like in the part of their molecular structures.

**[0010]** As examples for the acrylate bactericides as specified in the present invention, compounds (a) through (n) as described above can be preferably given. Considering C=X double bond contained in the acrylate bactericides, both E-type constitutional isomer and Z-type constitutional isomer can work as regard to the performance against carboxylates. Therefore, in case of the mixed compositions according to the present invention, any of purely E-type constitutional isomer, purely Z-type constitutional isomer and racemic mixture thereof can be used as a bactericide.

**[0011]** In the bactericidal compositions according to the present invention, a mixing ratio for a compound A represented by a general formula [I] and an acrylate compound B can be flexibly changed over a wide range, however, it is normally in a range of 1 : 0.01-1,000 on weight basis, and more preferably in a range of 1 : 100.

**[0012]** Further, the bactericidal compositions according to the present invention can be prepared into a formulation, such as oil solution, emulsifiable concentrate, wettable powder, granules, powder, aerosol, suspension concentrate, flowable concentrate, microcapsules, ULV, paste, etc. by mixing normally with solid carrier, liquid carrier, or gasificated carrier, and with a surfactant or other adjuvant for formulation. if appropriate. In the formulations described above, the active ingredients described above are preferably contained at a total rate of 0.1 to 99.9 % by weight , and more preferably at a total rate of 0.2 to 80 % by weight.

**[0013]** As examples for a solid carrier to be used for the preparation of formulations, clay, such as kaolinite, diatomaceous earth, synthesized silicon oxide hydrate, fubasami clay, bentonite and acid clay, talc, fine powder or granules of other inorganic minerals, such as sericite, silica powder, sulfur powder, activated carbon and potassium carbonate, can

be given, As examples for a liquid carrier to be used for the same, water, alcohols, such as methanol and ethanol, ketones, such as acetone, methyl ethyl ketone and cyclohexanone, aromatic hydrocarbons, such as toluene, xylene, ethyl benzene and methyl naphthalene, nonaromatic hydrocarbons, such as hexane, cyclohexane and kerosine, esters, such as ethyl acetate and butyl acetate, nitriles, acetinitrile and isobutylonitrile, ethers, dioxane and diisopropylether, acid amides, such as dimethylformamide and dimethylacetoamide, and halogenated hydrocarbons, such as dichloroethane and trichloroethane, can be given. As examples for a gas carrier, namely an injecting agent, carbon dioxide, butane gas, fluorocarbon, etc., can be given.

**[0014]** As examples for a surface active agent, alkylsulfate esters, alkylarylsulfates, alkylarylethers and their polyoxyethylenes, polyethyleneglycols, polyhydric alcohol esters. and sugar alcohol derivatives can be given. As examples for other inactive ingredients for formulation, a sticking agent and a dispersant, such as case in, gelatin, polysaccharides including starch, gum arabic, cellulose derivatives and alginic acid, lignin derivatives, bentonite and synthetic aqueous polymers including polyvinyl alcohol, polyvinyl pyrrolidone and polyacrylic acid, and a stabilizer, such as PAP (acidic isopropyl phosphate), BHT (2, 6-di-tert-butyl-4-methylphenol), BHA (2-/3-tert-butyl-4-methoxyphenol), vegetable oils, mineral oils, fatty acids and fatty acid esters, can be given.

**[0015]** The formulated bactericidal compositions according to the present invention can be applied either directly or following to dilution with water, etc. onto plants, water surface and soil. Furthermore, the inventive bactericidal compositions can be used in combination with any of other bactericides, insecticides, herbicides, fertilizers, soil reforming agents, etc. The dose of the bactericidal composition according to the present invention to be applied shall be variable depending upon each of a combination ratio of an active compound represented by a general formula [I] and a so-called acrylate bactericide, climatic condition, formulation type, time to apply, method to apply, place to apply, objective pest diseases, objective crops, etc., however, it is normally in a range of from 1 to 1,000 g as active component per ha, and more preferably in a range of from 10 to 100 g as the active components per ha. Whereas, the concentration of the bactericidal composition of the present invention preferably be applied, in case that the composition is formulated into any of emulsifiable concentrate, wettable powder, suspension concentrate and liquid and is applied following to dilution with water, it is normally in a range of from 1 to 1,000 ppm, and more preferably in a range of from 10 to 250 ppm. In case that the bactericidal compositions of the present invention are formulated into either granules or powder, it should be applied directly without preparing the diluted solution thereof.

Best Mode for Carrying Out the Invention

(Examples)

**[0016]** Now, the usefulness of the compositions of the present invention as a bactericide for controlling powdery mildew disease attacking various agricultural and horticultural crops is demonstrated with referring to the following Test Examples. The bactericidal activity of the compositions were evaluated by conducting a macroscopic observation on degrees of symptom of powdery mildew disease appeared on plant leaves at the time of assessment and comparing such symptoms of leaves with the one in plots for no-treatment. Whereas, for comparison purpose, a conventional emulsifiable concentrate formulation of the composition of the present invention was prepared by admixing compound A represented by a general formula [I] (Compound No. 1 in Table 1) and an acrylate bactericide B at a predetermined ratio.

Test Example 1: Test for controlling powdery mildew disease on wheat plants.

**[0017]** Emulsion prepared with the conventional emulsifiable concentrate formulated for the composition of the present invention to a predetermined concentration was sprayed onto young seedlings leaves of wheat plants (variety: Chihoku, 1-1.5 leaf stage) grown in a clay pot. After naturally drying the leaves at room temperature, the leaves were inoculated with the spores of Erysiphe graminis f. sp. tritici and were subjected to the infection for 7 days in a chamber maintained at approximately 22°C. The degree of symptoms caused by powdery mildew disease on the leaves were compared with the ones on leaves in the no-treatment plots to evaluate the preventing effectiveness of the composition, The results are shown in Table 2.

**[0018]** The effective degree E of the compositions of the present invention are calculated according to Corby' s formula (Weed., 15, 20-22, 1966) and is compared with the results, respectively.

$$E = x + y - \frac{x \cdot y}{100}$$

**[0019]** E is a value in percent as an expected effective degree when active compounds A and B were used at a con-

centration of m and n, respectively. X is a value in percent as an expected effective degree when active compound A was used at a concentration of m, whereas y is a value in percent as an expected effective degree when acitive compound B was used at a concentration of n.

Table 2

| Active Substance | Concentration of Active Substance in Spray Solution (ppm) | Actual Effective Degree(%) | Calculated Effective Degree (%) |
|---|---|---|---|
| Water (No treatment) | 0 | 0 | - |
| Compound A in W096/19442 (No. 1) | 0.2 | 13 | - |
| | 0.05 | 0 | - |
| Known Substance (1) | 0.05 | 38 | - |
| | 0.0125 | 19 | - |
| A + B | 0.2 + 0.05 | 81 | 41 |
| | 0.2 + 0.0125 | 30 | 30 |
| | 0.05 + 0.05 | 38 | 38 |

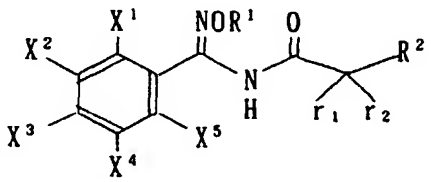
**[0020]** From the results as described above, it is understandable that the actual effective degree is more improved than the effective degree calculated according to Corby' s formula.

Industrial Use of the Invention:

**[0021]** It is an object of the present invention to provide bactericidal compositions which can excellently control plant diseases growing on various agricultural and horticultural crops, powder mildew disease, in particular.

## Claims

1. Fungicidal compositions characterized in that the composition comprises a benzamidoxime compound represented by a general formula [I];

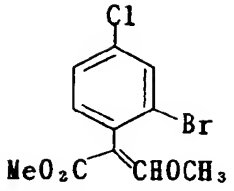


( I )

wherein $R^1$ represents optionally-substituted C1-C4 alkyl or optionally-substituted C2-C4 alkenyl, $R^2$ represents optionally-substituted phenyl or optionally-substituted heterocycle,

$X^1$ represents C1-C4 haloalkyl,
$X^2$, $X^3$, $X^4$ and $X^5$ each independently represent hydrogen, halogeno, C1-C4 alkyl, C1-C4 haloalkyl, C1-C4 alkoxy, C1-C4 haloalkoxy, C1-C4 alkylthio, C1-C4 alkylsulfinyl. C1-C4 alkylsulfonyl, nitro, amino or C1-C4 alkylcarbonylamino,
$r_1$ and $r_2$ each independently represent hydrogen, halogeno, C1-C4 alkyl, C1-C4 haloalkyl, C1-C4 alkoxy, C1-C4 alkylthio or amino, or $r_1$ and $r_2$ may get together to form carbonyl, and one or more than 2 compounds selected from a group consisting of compounds (a) through (n) as described below as the active ingredients.

(a)



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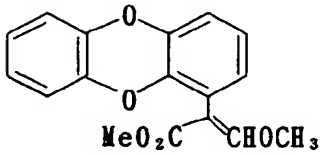

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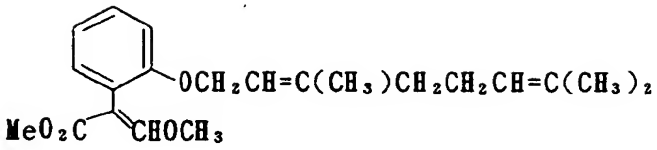
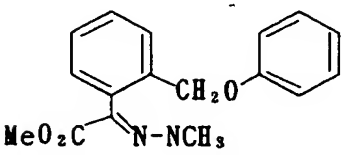
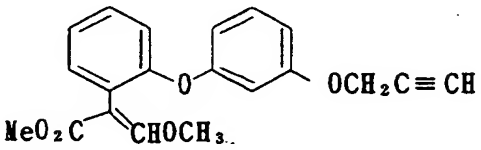


(d)



(e)



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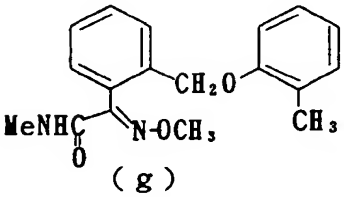
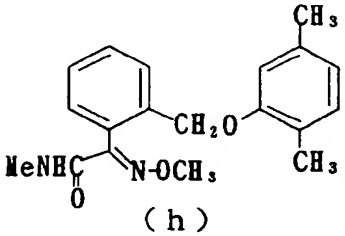


(g)



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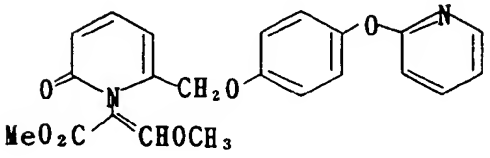
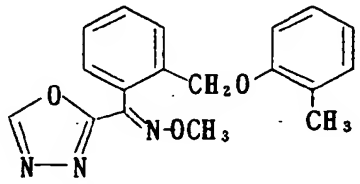


(i)



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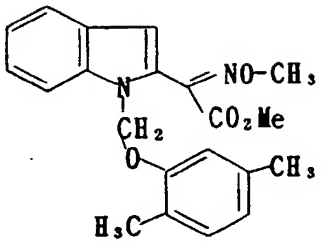
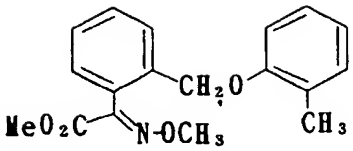
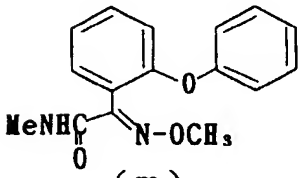


(k)



(l)



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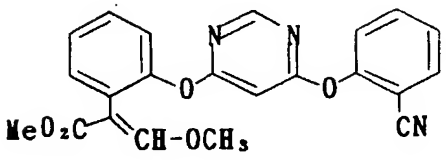

(n)

## INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP97/01880

A. CLASSIFICATION OF SUBJECT MATTER
Int. Cl$^6$ A01N37/52, A01N43/60, A01N37/36, A01N43/32, A01N37/38, A01N37/50, A01N43/40, A01N43/82, A01N43/38, A01N43/54
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
Int. Cl$^6$ A01N37/52, A01N43/60, A01N37/36, A01N43/32, A01N37/38, A01N37/50, A01N43/40, A01N43/82, A01N43/38, A01N43/54

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
CAS ONLINE

C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|---|---|---|
| A | JP, 2-6453, A (Nippon Soda Co., Ltd.), January 10, 1990 (10. 01. 90)(Family: none) | 1 |
| P,A | WO, 96/19442, A1 (Nippon Soda Co., Ltd.), June 27, 1996 (27. 06. 96) & AU, 9641895, A & ZA, 9603219, A | 1 |

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier document but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

| Date of the actual completion of the international search | Date of mailing of the international search report |
|---|---|
| August 13, 1997 (13. 08. 97) | August 26, 1997 (26. 08. 97) |
| Name and mailing address of the ISA/ Japanese Patent Office<br>Facsimile No. | Authorized officer<br>Telephone No. |

Form PCT/ISA/210 (second sheet) (July 1992)